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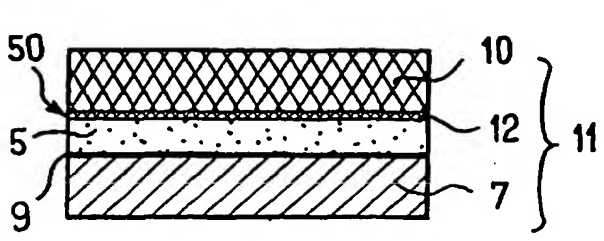
(54) Title: METHOD FOR MANUFACTURING A FREE-STANDING SUBSTRATE MADE OF MONOCRYSTALLINE SEMICONDUCTOR MATERIAL




(57) Abstract: The invention relates to a method for manufacturing a free-standing substrate made of monocrystalline semi-conductor material.This method is characterized by the following steps comprising: - transferring of a thin nucleation layer (5, 5') onto a support (7) by creating between the two a removable bonding interface (9) ;- growing by epitaxy on said thin nucleation layer (5, 5'), a microcrystalline layer (10) of material intended to comprise said substrate, until it attains a sufficient thickness to be free-standing, while preserving the removable character of the bonding interface (9) ; the coefficients of thermal expansion of the material of the thick layer (10) and of the support material (7) being chosen to be different from each other, such that at the time of cooling of the assembly, the stresses induced by differential thermal expansion between the support material (7) and that of the thick layer (10) causing the removal of said nucleation layer (5, 5') and said monocrystalline thick layer (10) from said support (7) at the level of said removable bonding interface (9).

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# METHOD FOR MANUFACTURING A FREE-STANDING SUBSTRATE MADE OF MONOCRYSTALLINE SEMI-CONDUCTOR MATERIAL

This invention relates to a method for manufacturing a free-standing substrate made of monocrystalline semi-conductor material, in particular a wide band gap material, and in particular a substrate comprised of gallium nitrate (GaN), aluminum nitrate (AlN) or of diamond.

A free-standing substrate is defined as a substrate, whose thickness is sufficient that it carries itself without support.

Reasonably, such a substrate must thus have a thickness of at least 100 µm. However, in order to be able to be manipulated in a manufacturing line without risk of breaking, it must generally be thicker.

By way of example, the commercially available free-standing substrates comprised of GaN or AlN have a thickness of 300 µm.

Such free-standing substrates comprised of GaN or AlN are used in opto-electronic devices such as LEDs, lasers, sensors or in micro-electronic devices

(transistors) or function in a high-temperature environment, or even in the field of hyperfrequency power or power electronics.

A first possibility for obtaining free-standing substrates can comprise fashioning them from a block of the material concerned by sawing and polishing.

Unfortunately, at the present time, there is no manufacturing method for GaN or AlN ingots on the industrial development scale.

The document "Bulk and homoepitaxial GaN growth and characterisation", Porowski-S, Journal of Crystal Growth, Vol. 189 - 190, June 1998, pp 153 - 158, describes a process for growing monocrystalline GaN ingot in liquid phase under a pressure of 12 to 20 kbars (12 to $20\times10^8$ Pa) and at a temperature of between 1400 and 1700 °C. These conditions are, however, difficult to implement in the course of mass production. In addition, they only allow crystals of a maximum diameter of 18 mm to be obtained.

Other teams of researchers have also worked on a method for growing the ingot in liquid phase at reduced pressure (less than 2 bars ($2\times10^5$ Pa)) and at a temperature of 1000 °C. The diameter of the crystals obtained is larger, in the vicinity of 50 mm, but the crystalline quality obtained is less satisfactory than in the previously mentioned method.

Finally, the document "Growth and characterisation of GaN single crystals", Balka *et al.*, Journal of Crystal Growth, Vol 208, January 2000, pp. 100 - 106, discloses the growth of monocrystalline GaN by

sublimation. The manufacturing conditions used are a pressure of less than 1 bar ($10^5$ Pa) and a temperature of from 1000 to 1200 °C. The crystal quality is very good but the size of the crystal is 3 mm, which is clearly inadequate for the intended applications.

At the present time, there is no monocrystalline gallium nitrate or aluminum nitrate on the market, in a massive form, of good quality, having sufficient diameters and at a reasonable price.

In order to resolve this problem, one notes in the literature a number of attempts at manufacturing substrates comprised of monocrystalline, free-standing gallium nitrate by thick heteroepitaxy and then eliminating the epitaxy substrate.

This thick epitaxy or hydride vapor phase epitaxy (known to the specialist in the art under the acronym HVPE, or "hydride vapor phase epitaxy") consists of producing epitaxial growth of GaN on diverse substrates between 1000 °C and 1100 °C at atmospheric pressure with a view to obtaining a layer of GaN of several tens or hundreds of microns.

This technique is advantageous in that it enables obtaining a good crystal quality and in that it is not necessary to face or to cut the ingots of crude material as in the aforementioned prior art. However, the GaN plates obtained in this fashion have many residual stresses and tensions connected with heteroepitaxy.

Several methods are distinguished according to the nature of the epitaxy support substrate and the technique used to remove said substrate.

Thus according to the document "Physical properties of bulk GaN crystals grown by HVPE", Melnik *et al.*, MRS Internet Journal of Nitride Semiconductor Research, Vol. 2, Art. 39, a method for growing GaN monocrystals using HVPE on a substrate comprised of monocrystalline silicon carbide (SiC) with removal of said substrate by reactive ionic etching (known to the person skilled in the art under the acronym RIE according to the English expression "reactive ionic etching"). However, removal of this SiC substrate is very time-consuming because it is chemically very inert.

Also, according to the document "Large free-standing GaN substrates by hydride vapor phase epitaxy and laser-induced lift-off," Kelly *et al.*, Jpn. J. Appl. Phys., Vol 38, 1999, a method for growing GaN by HVPE epitaxy on a sapphire substrate and subsequent removal of said substrate by laser is known (known by the English terminology, "laser-induced lift-off"). Implementing this removal technique is delicate for treating large surfaces because the laser beam scanning is long.

It is also possible to remove the sapphire substrate by mechanical polishing but this method is likewise time-consuming and further presents the risk of breakage of the GaN layer at the time of removal of the substrate that releases the stresses.

In other respects, the document "Preparation of large free-standing GaN substrates by hydride vapor phase epitaxy using GaAs as a starting substrate," Motoki *et al.*, Jpn. J. Appl. Phys., Vol. 40 (2001), pp. L140 - L143 describes a method for growing GaN on a substrate comprised of gallium arsenide (GaAs) by HVPE and then chemical dissolution of said substrate. This technique enables easy removal of the substrate, however, the latter is lost, which is less of an advantage from the economic point of view.

Other attempts have also been made by implementing a technique comprised of growing GaN or aluminum nitride (AlN) on a supporting substrate of silicon (Si {111} by HVPE and then removing the supporting substrate by chemical etching. This technique has the same drawbacks as those mentioned above.

Finally, according to the documents US-6,176,925, US 2001 / 0006845, US-2001 / 00022154 and EP-1 045 431 methods are known for obtaining a thick layer of gallium nitride by epitaxial techniques on a seed layer, itself having been obtained by epitaxy. However, none of the four documents teaches the possibility of placing a nucleation layer on a support by bonding by molecular adhesion.

The important points for realizing free-standing substrates are on the one hand the capacity of realizing thick epitaxy; that is, at least 100 microns while having good crystal quality and on the other hand easy separation of said thick layer from its epitaxy support.

The object of the invention is to remedy the aforementioned drawbacks while respecting these important points.

Said object is achieved in that the invention relates to a method for manufacturing a free-standing substrate made of microcrystalline semi-conductor material.

This method is remarkable in that it comprises the following constituent steps:

- transferring a thin nucleation layer on a support by creating between the two a removable bonding interface;

- growing by epitaxy on said thin nucleation layer, a microcrystalline layer of material intended to comprise said substrate until it attains a sufficient thickness to be free-standing, while preserving the removable character of the bonding interface,

the coefficients of thermal expansion of the material of the thick layer and of the support material being chosen to be different from each other, with a difference determined as a function of the temperature of epitaxial growth and a possible application of external mechanical stresses, such that at the time of cooling the assembly, starting from the epitaxial growth temperature, the stresses induced by differential thermal expansion between the support material and that of the thick layer, combined, if required, with said application of exterior mechanical stresses, causing the removal of said nucleation layer

and said monocrystalline thick layer from said support at the level of said removable bonding interface.

The method according to the invention also has the following advantageous characteristics, taken in isolation or in combination:

- the deposition of the thick layer by epitaxy is realized at least in part by hydride vapor phase epitaxy (HVPE);

- the thin nucleation layer is applied onto the support by direct bonding by molecular adhesion, the removable bonding interface being comprised of the contact surface between said thin nucleation layer and said support;

- before transferring the thin nucleation layer onto said support, a first intermediate bonding layer is applied onto at least one of the two, the removable bonding interface being comprised of the contact surface between on the one hand said first intermediate bonding layer and on the other hand the second intermediate bonding layer or said thin nucleation layer or said support;

- at least one of the intermediate bonding layer is a layer of silicon oxide ($SiO_2$);

- at least one of the intermediate bonding layer is a layer of silicon nitride ($Si_3N_4$);

- the bonding interface is made removable by effecting a treatment for augmenting the roughness of at least one of the two faces in contact at the level of said bonding interface;

- the treatment for augmenting the roughness of the surface is carried out by chemical attack or etching ;

- the bonding interface is made removable by effecting a treatment for decreasing the hydrophily of at least one of the two faces in contact with said bonding interface;

- the bonding interface is made removable by a thermal treatment using a thermal budget with a view of reducing the bonding energy between the two faces in contact at the level of said bonding interface;

- the method comprises, prior to the epitaxial growth of said thick layer, growing by means of epitaxy a fine nucleation layer on said nucleation thin layer ;

- said fine nucleation layer is produced by means of metal organic chemical vapor deposition (MOCVD) epitaxy or by molecular beam epitaxy (MBE);

- the external mechanical stresses applied at the time of removal are chosen from application of a jet of fluid, use of a blade or a guillotine;

- the method comprises the step of supplementary elimination of the nucleation layer that remains integral with the thick layer intended to form the free-standing substrate;

- prior to transferring the thin nucleation layer onto said support, the nucleation layer is formed by implantation of atomic species at the interior of a source substrate, in the vicinity of a defined depth, in such a fashion as to define at said depth an

embrittlement zone separating said nucleation layer from the rest of the source substrate;

- the support is monocrystalline or polycrystalline and is chosen from silicon carbide, silicon, sapphire, gallium nitride or aluminum nitride;

- the monocrystalline material comprising said free-standing substrate is a wide band gap material;

- the wide band gap material is gallium nitride (GaN);

- the wide band gap material is aluminum nitride (AlN);

- the thin nucleation layer is realized using a monocrystalline material chosen from gallium nitride, silicon, silicon carbide, sapphire, diamond or aluminum nitride;

- the thick layer is realized in diamond and the nucleation layer is realized in diamond, silicon or silicon carbide.

Other aspects, objects and advantages of the invention will emerge on reading the detailed description that follows. This description will be better understood when read with reference to the annexed drawings, wherein:

- Figures 1 to 6 are representations illustrating different series of successive stages of the method according to the invention and their variants.

In these figures it will be noted that the different layers are not represented in their actual scale, especially as concerns their thickness.

The method in its entirety will first be briefly described.

This method comprises:

- bonding a seed layer or "nucleation layer" on a mechanical support by means of a removable bonding interface, then

- growing, by epitaxy, on said nucleation layer, a thick layer of the material comprising the substrate that is to be obtained, by thus forming a stack of layers and then

- removing said thick layer and said nucleation layer, from the mechanical support, at the level of said removable bonding layer, in particular by imposing thermal stresses associated to the gap between the thermal expansion coefficients of the different layers constituting said stack, and eventually mechanical stresses.

The process will now be described in more detail.

Figure 1 represents a first variant for obtaining the nucleation layer.

The purpose of the method according to the invention is the manufacture of the free-standing substrates in a monocrystalline semi-conductor material, particularly in a material having a wide band gap, and particularly among those, substrates comprised of

gallium nitride (GaN) or aluminum nitride (AlN), or under certain conditions even diamond.

In order to prepare the nucleation layer, a source substrate 1 is chosen, whose nature and crystal lattice parameters enable the subsequent growth by epitaxy of the thick layer constituting the future free-standing substrate.

Consequently, one can chose in a particularly appropriate fashion as the source substrate 1, a monocrystalline material among gallium nitride (GaN), silicon (Si); silicon carbide (SiC), sapphire, diamond or aluminum nitride (AlN).

It should be noted that when the free-standing substrate is made of diamond, the nucleation layer should preferably also be made of diamond, silicon or silicon carbide.

An atomic species implantation operation 3 is carried out on one of the flat surfaces of this substrate 1, called the frontal face 2.

Implantation of an atomic species is defined as any bombardment of atomic, molecular, or ionic species capable of introducing said species into a material with a maximum of concentration of said species in the material, said maximum being at a defined depth with respect to the bombarded surface 2. The atomic, molecular or ionic species is introduced into the material using an energy equally distributed around a maximum.

The implantation of the atomic species into said source substrate 1 can be done, for example, using an ion beam implanter or a plasma immersion implanter.

Preferably, this implantation is done by ionic bombardment. Preferably, the ionic species implanted is hydrogen. Other ionic species can be advantageously used alone or in combination with hydrogen, such as rare gases (helium, for example).

This implantation has the effect of creating in the volume of the source substrate 1 and at an average depth of ion penetration, an embrittlement zone 4 separating said substrate 1 into two parts.

On this subject, reference is made to the literature concerning the method known under the Smart Cut registered trademark.

The embrittlement zone 4 formed in this fashion delimits the one layer 5 corresponding to the upper part of the substrate 1 and extending from the bombarded surface 2 to said embrittlement zone 4 and a lower part corresponding to the rest of the source substrate 1. This layer 5 will constitute later the nucleation layer.

By way of example, the energy of implantation that can be obtained using the equipment currently available in micro-electronics is such that the maximal thickness of the nucleation layer 5 is of the order of 0.5 μm to 1.5 μm. Using more powerful implanters it is possible to obtain a thicker layer 5.

Figures 2A and 2B represent a variant for obtaining the nucleation layer.

The source substrate 1 used is identical to that described above.

A so-called porosification treatment 6 is effected on the frontal surface 2'. By way of example, one can refer to EP 0 849 788, which describes such a process.

Then one proceeds with the epitaxial growth on this frontal surface 2' of a supplemental layer 5' of a material preferably identical to that of the source substrate 1.

The porosification treatment thus enables forming a layer or embrittled zone 4' imbedded between the source substrate 1 and said layer 5'; this latter constituting the future nucleation layer.

Figures 3A to 3C represent the application of the nucleation layer 5 on the support 7. In these figures, as well as in Figures 4 to 6, for the sake of simplification, only the nucleation layer showing numeral reference 5 is represented; in other words, that one obtained by the method represented in Figure 1. However, it is quite obvious that it could also be the layer referenced using 5', obtained by the porosification method described in conjunction with Figures 2A and 2B or by any other similar method.

In a first variant embodiment represented in Figure 3B, the bonding between the nucleation layer 5 and the support 7 is made by molecular adhesion. These bonding techniques are known to the specialist in the art and are described, for example, in the paper by

Gosële, "Semiconductor wafer bonding", Sciences and Technology, Q.Y. Tong, U. Gosële, Wiley Interscience Publications.

In a second variant embodiment, represented by Figures 4A and 4B, the bonding is done by application of a first intermediate bonding layer 8 on the nucleation layer 5 and a second intermediate bonding layer 8' on the support 7, then bonding of the two intermediate layers 8 and 8' on each other by molecular adhesion as hereinbefore described.

Finally, in a third variant embodiment (not represented in the figures), a single intermediate bonding layer 8' is applied on the support 7 and then bonded on top of the nucleation layer 5 or, inversely, a single intermediate bonding layer 8 is applied on the nucleation layer 5 and it is then bonded on top of the support 7.

These bonding layers 8, 8' are of a thickness in the area of 0.5 μm and are advantageously layers of oxide, for example, $SiO_2$ or nitride, for example $Si_3N_4$, deposited by chemical vapor deposition. It is also possible to intercalate between the support 7 and the layer 5 of the intermediate bonding layers 8, 8' of different types, for instance, one layer of oxide and one layer of nitride.

The support 7 and the nucleation layer 5 are assembled by way of a bonding interface referenced using 9.

Bonding interface is defined as the contact surface between two facing surfaces, assembled with each other by bonding.

According to the different cases mentioned above, it can be either the contact surface between the frontal surface 2 of the nucleation layer 5 and the frontal face 70 of the support 7 (see Figures 3A and 3B) or the contact surface between the respective frontal surfaces 80, 80' of the two intermediate bonding layers 8 and 8'(see Figures 4A and 4B).

Finally, when one single intermediate bonding layer is applied between the nucleation layer 5 and the support 7, the bonding interface 9 is then the contact surface between said intermediate layer and, depending on the situation, the frontal face 2 of the nucleation layer 5 or the frontal face 70 of the support 7 which was bonded on said intermediate layer.

According to one important characteristic of the invention, this bonding interface 9 is removable.

This means that a treatment is effected prior to the molecular adhesion bonding step, which is intended to reduce the bonding energy level at the bonding interface 9 in such a fashion as to bring it to a level lower than that obtained by normal bonding.

In the course of the description and the claims, the expression 'normal bonding' is defined as an operation comprising classical bonding by molecular adhesion of two surfaces against each other after normal preparation of said surfaces; in other words, cleaning in baths of chemical products then thermal

annealing; for more information on this subject see the following publications: C. Maleville *et al.*, Semiconductor wafer bonding, Science Electrochemical Society Proceeding Series, Permington, NJ (1998) and O. Rayssac *et al.* "Proceeding of the 2nd International Conference on Materials for Microelectronics," IOM Communications, p. 183, 1998.

Of course, the value of this bonding energy is a function of the nature of the materials in contact along said bonding interface, of the temperature at which said molecular adhesion bonding is effected, and of the temperature at which the thermal annealing is effected.

By way of purely illustrative example, in the case of bonding of a layer of $SiO_2$ to another layer of $SiO_2$, the bonding energy between the two layers of $SiO_2$ is in the area of 100 mJ / $m^2$ for bonding done at ambient temperature and after normal preparation of the surfaces and can attain 1 to 2 J / $m^2$ after annealing treatments between 400 and 1100 °C. After treatment intended to reduce the bonding energy level, by example by roughening as described above, all of the other parameters being otherwise identical, the roughness is in the area of 0.625 nm RMS and the bonding energy after the annealing cycle at 100 °C is in the area of only 500 mJ / $m^2$.

Identical values are obtained using $SiO_2$ / Si bonding.

At the time of removal, disassembling is necessarily effected in the plane of the bonding

interface 9 and not irregularly along a fracture line that would at times extend into one of the opposing surfaces or into the opposing face, or between the two.

Various examples of treatment methods enabling reduction of the bonding energy level and making the bonding interface 9 removable will now be described.

A first method consists of increasing the roughness of at least one of the two faces in contact. This increase of the roughness can be done locally by chemical attack or etching using hydrofluoric acid (HF), for instance; see the article by O. RAYSSAC *et al.*, for example.

A second method consists in reducing the hydrophily of the surfaces to be brought into contact, prior to the actual bonding, by chemical cleaning using the methods, for example, as described in the article by C. Maleville captioned above.

A third method for obtaining a removable bonding interface consists in reducing the thermal budget normally sufficient to achieve bonding energies currently obtained by standard bonding. The thermal budget corresponds to the temperature of a thermal treatment multiplied by the duration of the treatment.

Finally, it should be noted that it is possible to utilize the aforesaid methods alone or in combination.

As concerns the support 7, this plays essentially a mechanical support role. It is advantageously chosen from silicon carbide, silicon, sapphire, gallium nitride or aluminum nitride.

Then the nucleation layer 5 is detached from the rest of the source substrate 1 along the embrittlement zone 4 (see Figures 3B and 3C or 4B and 4C). The exposed top surface of said nucleation layer 5 is indicated by the numerical reference 50.

In order to allow the detachment along said embrittlement zone 4 and not along the bonding interface 9, it is necessary that said embrittlement zone 4 has a mechanical strength lower than that of said bonding interface 9.

In the case wherein the embrittlement zone 4 is formed by hydrogen implantation, detachment is effected either solely under the action of the application of an appropriate thermal budget by heating the layer stack formed at a sufficient temperature so as to induce detachment (typically 500 °C for silicon and 900 °C for silicon carbide), or by the application of external mechanical stresses with or without the joint application of a thermal budget.

It should be noted that the thermal budget applied must, however, be limited in such a fashion as to conserve the removable character of the bonding interface 9.

Application of a mechanical stress can consist in exerting a bending and / or traction force on the posterior part of the source substrate 1 or introducing at the embrittlement zone 4 a blade or a jet of fluid (gas or liquid), for example. It can also take the form of application of shearing or ultrasound forces.

The external mechanical stresses can also be of electrical energy origin deriving from the application of an electrostatic or electromagnetic field.

Finally, the external mechanical stresses can also be of thermal energy origin deriving from the application of an electromagnetic field, an electron beam, thermoelectric heating, a cryogenic fluid, a super-cooled liquid, etc.

After detachment along the embrittlement zone 4, stack comprised of the mechanical support 7 and the nucleation layer 5 is obtained, between which one (or a plurality) of intermediate bonding layer(s) 8, 8' (see Figures 3C or 4C) may be intercalated.

A finishing operation can be operated on the exposed top surface 50 of the nucleation layer 5 in order to improve the compatibility of said surface with the subsequent epitaxial growth. This finishing operation can be done by polishing, etching or thermal treatment and, in the last-mentioned case, it is assured that the application of the additional thermal budget does not destroy the removable character of the bonding interface 9.

Other techniques for obtaining the nucleation layer 5 on the support 7 are well known to the person skilled in the art and can also be utilized.

For example, one technique derived therefrom can be cited, which enables obtaining substrates of the type known to the person skilled in the art under the acronym BESOI or 'bond an etch back silicon on insulator' or also BSOI, 'bonded SOI'.

These techniques consist in bonding the source substrate 1 directly onto the support substrate 7 and then proceeding with physical removal of the back of the source substrate either by polishing techniques or by chemical etching techniques until a layer 5 of the desired thickness is obtained.

As illustrated in Figures 5A and 6A, a thick layer 10 of the monocrystalline substrate that one wishes to obtain is then deposited on the exposed upper surface 50 of the nucleation layer 5. Thus, a stack (reference 11) is obtained.

Advantageously, this thick layer 10 deposit is effected by epitaxy and at least partly by means of hydride vapor phase epitaxy (known to the person skilled in the art under the acronym HVPE or 'hydride vapor phase epitaxy').

This deposit is effected at a temperature between 1000 and 1100 °C, preferably 1050 °C. Care is taken to maintain this temperature in a range of values allowing preservation of the removable character of the bonding interface 9.

This deposit is continued until achieving a sufficient thickness that the layer 10 is ultimately free-standing when it is removed from the support 7.

The method of realizing this epitaxy, the parameters and the respective orientation of the nucleation layer and the thick layer are known to the specialist in the art.

According to one embodiment of the invention represented only in Figures 5A and 5B for the sake of

simplification but which could also be done using the method variant represented in Figures 6A to 6C, it is also possible to proceed, prior to deposit of said thick layer 10, with a growth phase by means of epitaxy of a fine nucleation layer 12. This can be done using the same material as that used subsequently for the realization of the thick layer 10 but not necessarily identical to that of the nucleation layer 5.

This step can be advantageous for improving the crystal quality of the thick layer 10.

In this instance, and particularly for GaN, epitaxy of this fine layer can be realized by metal organic chemical vapor deposition (known to the specialist in the art under the acronym MOCVD) or by molecular beam epitaxy (known to the specialist in the art under the acronym MBE).

It is also possible to use lateral growth techniques known to the specialist in the art under the acronym ELOG or epitaxial lateral over-growth.

According to another embodiment, the material used to form the fine nucleation layer 12 can also be different from that used for the thick layer 10 and for the nucleation layer 5. By way of example, a fine epitaxial layer of AlN can be deposited on a nucleation layer of SiC prior to growth of a thick layer of GaN. The formation techniques used for the fine epitaxial layer are identical to those hereinbefore described.

As illustrated in Figures 5B and 6B, the support 7 and the intermediate bonding layer 8', if present, is then removed from the rest of the stack comprised of

the nucleation layer 5 and the thick layer 10, and eventually from the bonding layer 8.

This removal is done along the removable bonding interface 9.

The coefficients of thermal expansion are fixed values established for a given material. However, the expansion of the material and its elastic energy depend on its thickness. In a stack of layers, the behavior of the different layers is dictated in a first approximation by the thickest layer(s). In the present case, the nucleation layer 5 has a thickness of several microns, whilst the thick layer 10 is more in the area of 100 µm or even 200 µm and the support is at least 300 µm thick. Consequently, in the first approximation the thermal expansion coefficients of the support 7 and those of the thick layer 10 are taken into account in order to predict the removal behavior of these two layers. At the second level, the presence and the nature of the intermediate bonding layer(s) can be significant for the distribution of the stresses in the structure considered.

In other words, if as a result of the nature of the materials chosen for the support 7 and the thick layer 10, the gap between their coefficients of thermal expansion is significant, removal is then done naturally, along the removable bonding interface 9, when the temperature of the stacking 11 decreases, after epitaxy realized between 1000 and 1100 °C. When, on return of the stack 11 to ambient temperature (around 20 to 25 °C) or even at a temperature of

between the temperature of epitaxy and ambient temperature, stresses appear at the interior of the stack such that the removal is done naturally in the plane of the removable bonding interface 9, which constitutes a zone, wherein the bonding forces are lower than normal.

If, on the other hand, the gap between the coefficients of thermal expansion of the support 7 and of the thick layer 10 is small, then the aforesaid stack 11 will be more mechanically stabile and removal or disassembly will require additional application of exterior mechanical stresses. These stresses are identical to those mentioned above for the detachment along the embrittlement zone 4.

Finally, elimination of the nucleation layer 5 is effected (see Figures 5C and 6C) by polishing, ionic etching or by attack using a chemical solution, for example. The choice of the technique used is a function of the nature of the material of the layer 5.

Later, it is also possible to realize a finishing step comprising removal of several tens of microns from the part of the thick layer 10 that is situated in contact with said nucleation layer 5. The support 7 can also be recovered and recycled.

Four exemplary embodiments of the method of the invention are now described in detail.

EXAMPLE 1: Manufacturing of a free-standing GaN substrate using an intermediate stack comprising a silicon Si support, two intermediate $SiO_2$ / $SiO_2$

bonding layers and a monocrystalline GaN nucleation layer.

A monocrystalline gallium nitride (GaN) nucleation layer 5 is formed in a source substrate 1 of solid GaN by ion implantation. This nucleation layer 5 is bonded onto a silicon mechanical support 7 by two intermediate bonding layers 8, 8' of $SiO_2$ bonded together along a bonding interface 9.

Prior to being assembled together, the two intermediate layers 8, 8' undergo mechano-chemical planarization and surface treatment intended to increase roughness of the opposing surfaces 80, 80' (treatment with hydrofluoric acid HF or with a chemical cleaning solution known to the specialist in the art by the name SC1 and comprised principally of ammonia diluted with hydrogen peroxide $H_2O_2$).

Then the nucleation layer 5 is detached from the rest of the substrate 1 along the embrittlement zone 4 using a thermal treatment done at 900 °C.

Thermal treatment for stabilization of the bonding interface 9 is done at 950 °C over 2 hours; in other words, at a temperature slightly higher than that currently used for bonding of this type. The bonding interface 9 is thus removable.

Then a surface finishing step is done on the exposed surface 50 of the nucleation layer 5.

One then proceeds with rapid growth of a GaN layer 10 using HVPE at 1050 °C. At this temperature, the bonding interface 9 is slightly reinforced but has,

however, bonding forces greatly lower than the standard bonding energies (that is, around 1 to 2 J / $m^2$).

When the GaN attains a thickness of 200 µm; that is a thickness sufficient to be ultimately free-standing, deposition is stopped and the stack of the layers obtained is brought to ambient temperature.

The silicon support 7, whose thickness is greater than 300 µm is chosen in order to have a coefficient of thermal expansion of $2.5\times10^{-6}$ / K, whilst that of the GaN epitaxial thick layer 10 is in the area of $5.6\times10^{-6}$ / K.

Consequently, the mechanical strength of the stack thus formed is low and disassembly along the bonding interface 9 is done spontaneously when the temperature of the stack, which had reached 1050 °C during the epitaxy process, decreases.

Elimination of the $SiO_2$ layers, the GaN nucleation layer 5, or even several micrometers from the GaN thick layer 10 is effected by finishing polishing in order to give it the characteristics of a wafer.

EXAMPLE 2: Manufacturing of a free-standing AlN substrate using an intermediate stack comprising a silicon Si support, intermediate $SiO_2$ / $SiO_2$ bonding layers and a monocrystalline AlN nucleation layer.

One proceeds in identical fashion as described for Example 1, except that the gallium nitride is replaced by aluminum nitride (AlN) and that the different AlN layers have a coefficient of thermal expansion in the area of $4.15\times10^{-16}$ / K, whilst the coefficient of

thermal expansion of the silicon forming the support is $2.5\times 10^{-6}$ / K.

Removal is done likewise naturally by lowering the temperature of the stack.

EXAMPLE 3: Manufacturing of a free-standing GaN substrate using an intermediate stack comprising a silicon support, a single intermediate bonding layer of $SiO_2$ and a silicon Si {111} nucleation layer.

A nucleation layer 5 of silicon {111} is formed in a source substrate 1 of the same type by ion implantation. This nucleation layer 5 is bonded onto a silicon mechanical support 7 by an intermediate bonding layer 8 of $SiO_2$ obtained by thermal oxidation of the top surface of the source substrate 1. The bonding interface 9 is disposed between the top surface 80 of the $SiO_2$ layer and the frontal surface 2 of the nucleation layer 5.

This bonding interface 9 is treated as in Example 1 so as to be removable.

Then the nucleation layer 5 is removed from the rest of the substrate 1 along the zone of embrittlement 4.

A finishing step is then operated on the exposed surface 50 of the nucleation layer 5.

Then fast growth of a GaN layer 10 by HVPE at 1050 °C is realized. At this temperature, the bonding interface 9 is slightly reinforced but has, however, lower than normal bonding forces.

When the GaN attains a thickness of 200 µm; that is, a thickness sufficient so as to be ultimately free-standing, deposition is stopped and the stack of layers is brought to ambient temperature.

The silicon support 7, whose thickness is greater than 300 µm is chosen to have a coefficient of thermal expansion of is $2.5 \times 10^{-6}$ / K, whilst that of the thick layer of epitaxial GaN is in the area of is $5.6 \times 10^{-6}$ / K.

Consequently, the mechanical strength of the stack so formed is low and removal along the bonding interface 9 is done spontaneously when the temperature of the stack, which had reached 1050 °C during epitaxy, decreases.

One then proceeds with the elimination of the Si {111} nucleation layer 5 as described in Example 1.

EXAMPLE 4: Manufacturing of a free-standing GaN substrate using an intermediate stack comprising a silicon support, two intermediate $SiO_2$ / $SiO_2$ bonding layers, a monocrystalline SiC nucleation layer and a supplementary fine epitaxial monocrystalline GaN layer.

A nucleation layer 5 of monocrystalline silicon carbide (SiC) is formed in a source substrate 1 of solid SiC by ion implantation. This nucleation layer 5 is bonded onto a silicon mechanical support 7 by two intermediate bonding layers 8, 8' of $SiO_2$ bonded to each other along a bonding interface 9.

This bonding interface 9 is treated as described in Example 1 in such a manner as to be removable and

the nucleation layer 5 is detached from the rest of the substrate 1.

A finishing step is then operated on the exposed surface 50 of the nucleation layer 5.

Then a fine layer 12 of GaN having a thickness of less than 3 or 4 μm is deposited by epitaxial growth by MOCVD. This deposit is done either uniformly over the entire surface of the nucleation layer or locally to achieve the effects of lateral growth (ELOG). Then the layer stack thus formed is allowed to cool until it reaches ambient temperature (around 20 °C).

Then fast growth of a GaN layer 10 by HVPE at 1050 °C is realized. At this temperature, the bonding interface 9 is slightly reinforced but has, however, lower than normal bonding forces (around 2 J / $m^2$).

When the GaN attains a thickness of 200 μm; that is, a thickness sufficient so as to be ultimately free-standing, deposition is stopped and the stack of layers is brought to ambient temperature.

The silicon support 7, whose thickness is in the area of 300 to 400 μm is chosen to have a coefficient of thermal expansion in the area of is $2.5\times10^{-6}$ / K, whilst that of the thick layer of epitaxial GaN is in the area of is $5.6\times10^{-6}$ / K.

Consequently, the mechanical strength of the stack so formed is low and removal or disassembly along the bonding interface 9 is done spontaneously when the temperature of the stack decreases.

A finishing step is then operated as described in Example 1.

EXAMPLE 5: Manufacturing a free-standing diamond substrate using an intermediate stack comprising a silicon Si support, two intermediate $SiO_2$ / $SiO_2$ bonding layers and a diamond nucleation layer.

A nucleation layer 5 of diamond is formed in a source substrate 1 of high crystal quality monocrystalline diamond by ion implantation. This nucleation layer 5 is bonded onto a silicon mechanical support 7 by two intermediate bonding layers 8 of $SiO_2$.

The bonding interface 9 is disposed between the two surfaces 80, 80' of the $SiO_2$ layers. It is treated as described in Example 1 so as to be removable.

Then the nucleation layer 5 is removed from the rest of the substrate 1 along the embrittlement zone 4; one then proceeds with a finishing step of the exposed surface 50.

Then fast growth of a diamond layer 10 by CVD (chemical vapor deposition) at between 800 and 1000 °C is realized. At this temperature, the bonding interface 9 is slightly reinforced but has, however, lower than normal bonding forces.

When the diamond attains a thickness of 200 µm; that is, a thickness sufficient so as to be ultimately free-standing, deposition is stopped and the stack of layers is brought to ambient temperature.

The silicon support 7, whose thickness is greater than 300 µm is chosen to have a coefficient of thermal

expansion of is $2.5 \times 10^{-6}$ / K, whilst that of the thick layer of diamond is in the area of is $1 \times 10^{-6}$ / K.

Consequently, the mechanical strength of the stack so formed is relatively high and disassembly along the bonding interface 9 cannot be done solely spontaneously when the temperature, which attained 800 to 1000 °C during epitaxy, of the stack decreases. It is necessary to force the separation by using a guillotine.

One then proceeds with the removal of the diamond nucleation layer 5 as described in Example 1.

## CLAIMS

1. A method for manufacturing a free-standing substrate (10) made of monocrystalline semi-conductor material, characterized in that it comprises the following steps comprising:

- transferring of a thin nucleation layer (5, 5') onto a support (7) by creating between the two a removable bonding interface (9) ;

- growing by epitaxy on said thin nucleation layer (5, 5'), a microcrystalline layer (10) of material intended to comprise said substrate, until it attains a sufficient thickness to be free-standing, while preserving the removable character of the bonding interface (9) ;

the coefficients of thermal expansion of the material of the thick layer (10) and of the support material (7) being chosen to be different from each other with a difference determined as a function of the temperature of epitaxial growth and a possible application of external mechanical stresses, such that at the time of cooling of the assembly, starting from the epitaxial

growth temperature, the stresses induced by differential thermal expansion between the support material (7) and that of the thick layer (10), combined, if required, with said application of exterior mechanical stresses, causing the removal of said nucleation layer (5, 5') and said monocrystalline thick layer (10) from said support (7) at the level of said removable bonding interface (9).

2. The method according to Claim 1, wherein the deposition of the thick layer (10) by epitaxy is realized at least in part by hydride vapor phase epitaxy (HPVE).

3. The method according to Claim 1 or 2, wherein the thin nucleation layer (5, 5') is applied onto the support (7) by direct bonding by molecular adhesion, the removable bonding interface (9) being comprised of the contact surface between said thin nucleation layer (5, 5') and said support (7).

4. The method according to Claim 1 or 2, wherein prior to transferring the thin nucleation layer (5, 5') onto said support (7), a first intermediate bonding layer (8, 8') is applied to at least one of the two, the removable bonding interface (9) being comprised of the contact surface between on the one hand said first intermediate bonding layer (8, 8') and on the other hand the second intermediate bonding layer (8', 8) or said thin nucleation layer (5, 5') or said support (7).

5. The method according to Claim 4, wherein at least one of the intermediate bonding layers (8, 8') is a layer of silicon oxide ($SiO_2$).

6. The method according to Claim 4 or 5, wherein at least one of the intermediate bonding layers (8, 8') is a layer of silicon nitride ($Si_3N_4$).

7. The method according to at least one of the above claims, wherein the bonding interface (9) is made removable by effecting a treatment for augmenting the roughness of at least one of the two faces (2, 80 ; 80', 70) in contact at the level of said bonding interface (9).

8. The method according to Claim 7, wherein the treatment for augmenting surface roughness is carried out by chemical attack or etching.

9. The method according to at least one of the above claims, wherein the bonding interface (9) is made removable by effecting a treatment for decreasing the hydrophily of at least one of the two surfaces (2, 80 ; 80', 70) in contact at the level of said bonding interface (9).

10. The method according to at least one of the above claims, wherein the bonding interface (9) is made removable by thermal treatment using a thermal budget with a view of reducing the bonding energy between the two faces (2, 80 ; 80', 70) in contact at the level of said bonding interface (9).

11. The method according to at least one of the above claims, wherein it comprises, prior to the epitaxial growth of said thick layer (10), growing by means of epitaxy a fine nucleation layer (12) on said thin nucleation layer (5, 5').

12. The method according to Claim 11, wherein said fine nucleation layer (12) is produced by means of

metal organic chemical vapor deposition (MOCVD) epitaxy or by molecular beam (MBE) epitaxy.

13. The method according to at least one of the above claims, wherein the external mechanical stresses applied at the time of removal are chosen from application of a jet of fluid, the use of a blade, or a guillotine.

14. The method according to at least one of the above claims, wherein it comprises the step of supplementary elimination of the nucleation layer (5, 5') that remains integral with the thick layer (10) intended to form the free-standing substrate.

15. The method according to at least one of the above claims, wherein, prior to transferring the thin nucleation layer (5, 5') onto said support (7), the nucleation layer (5, 5') is formed by implantation (3) of an atomic species at the interior of a source substrate (1), in the vicinity of a defined depth, in such a fashion as to define at that depth an embrittlement zone (4) separating said nucleation layer (5, 5') from the rest of the source substrate (1).

16. The method according to at least one of the above claims, wherein the support (7) is monocrystalline or polycrystalline and is chosen from silicon carbide, silicon, sapphire, gallium nitride or aluminum nitride.

17. The method according to at least one of the above claims, wherein the monocrystalline material comprising said free-standing substrate (10) is a wide band gap material.

18. The method according to Claim 17, wherein the wide band gap material is gallium nitride (GaN).

19. The method according to Claim 17, wherein the wide band gap material is aluminum nitride (AlN).

20. The method according to at least one of the above claims, wherein the thin nucleation layer (5, 5') is realized using a monocrystalline material chosen from gallium nitride, silicon, silicon carbide, sapphire, diamond or aluminum nitride.

21. The method according to at least one of Claims 1 to 16, wherein the thick layer (10) is realized in diamond and the nucleation layer (5, 5') is realized in diamond, silicon or silicon carbide.

FIG.1

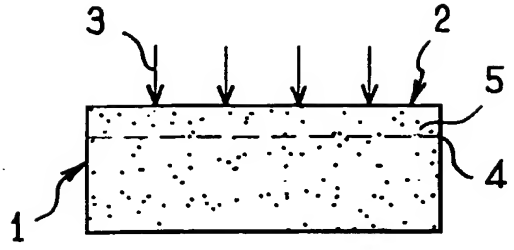


FIG.2A

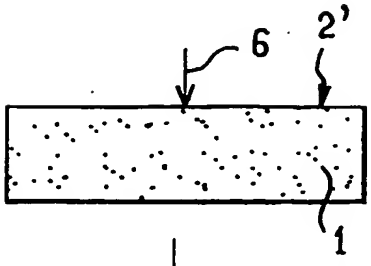


FIG.2B

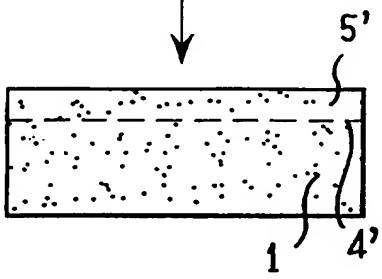


FIG.3A

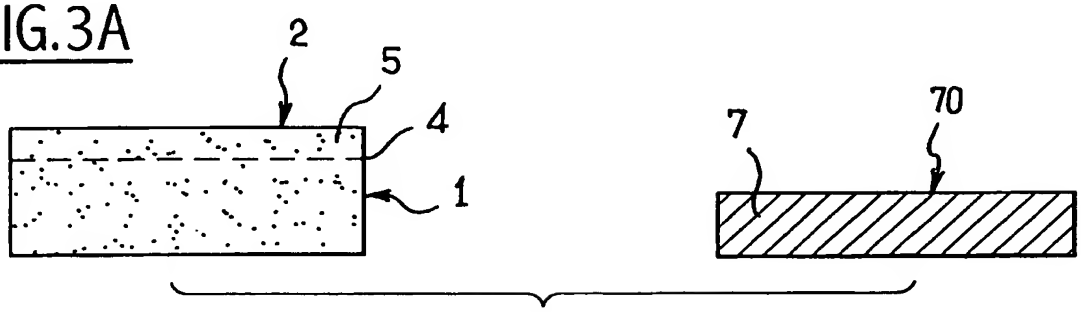


FIG.3B

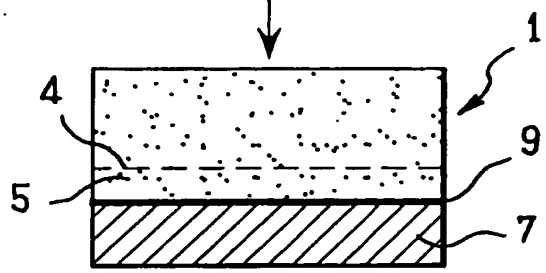


FIG.3C

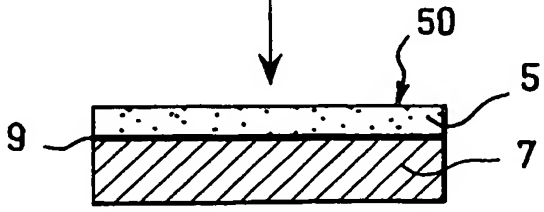

FIG.4A

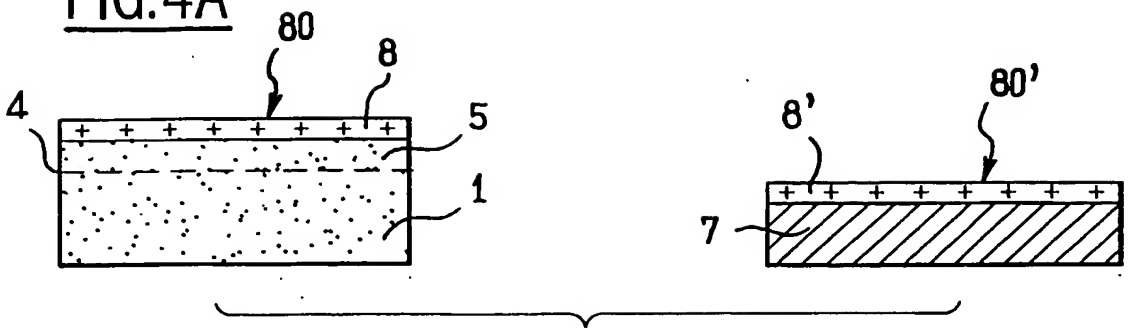


FIG.4B

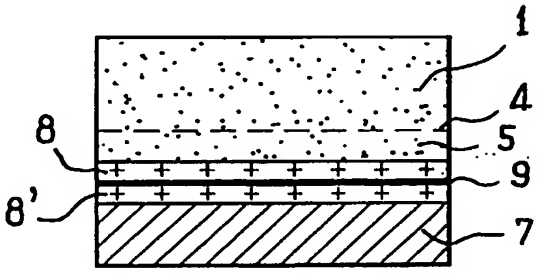


FIG.4C

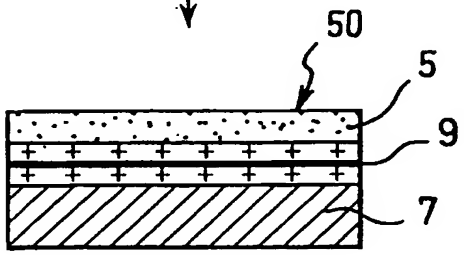

FIG.5A

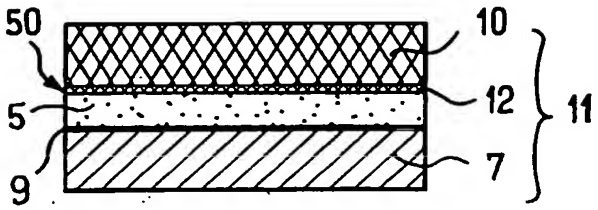


FIG.5B

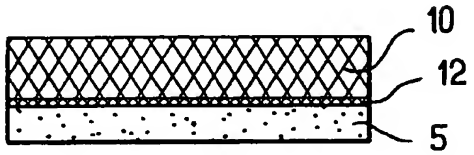


FIG.5C


FIG.6A

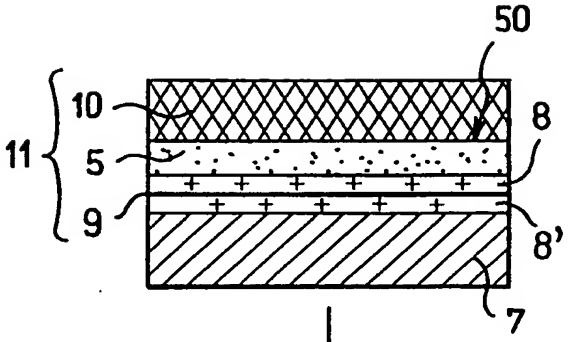


FIG.6B

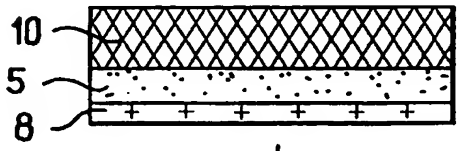


FIG.6C

# INTERNATIONAL SEARCH REPORT

Internati· Application No
PCT/EP 03/00693

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C30B29/40 C23C16/27 H01L21/20

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 H01L C23C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category ° | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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| Date of the actual completion of the international search | Date of mailing of the international search report |
|---|---|
| 28 July 2003 | 05/08/2003 |

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| European Patent Office, P.B. 5818 Patentlaan 2<br>NL – 2280 HV Rijswijk<br>Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,<br>Fax (+31-70) 340-3016 | Le Meur, M-A |

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# INTERNATIONAL SEARCH REPORT

Internat application No
PCT/EP 03/00693

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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